

924,601



Date of Application and filing Complete Specification: Aug. 8, 1960.

No. 27493/60.

Two Applications made in Germany (Nos. F29145 IVb/22a and F29146 IVb/22a) on Aug. 8, 1959.

Complete Specification Published: April 24, 1963.

Index at acceptance:—Class 2(4), P9A(3A2:3C1:4F), PD1J.

International Classification:—C09b.

COMPLETE SPECIFICATION

Basic Heterocyclic Azo Dyestuffs

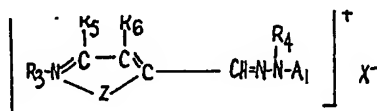
SPECIFICATION NO. 924,601

The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act 1949 is Roderich Raue, Heymannstrasse 49, Leverkusen, Germany, of German nationality.

THE PATENT OFFICE

DS 72370/1(7)/R.109 200 3/83 PL

- 10 This invention is concerned with new basic dyestuffs and with the production thereof. In Specification No. 27,393/58 (Serial No. 875,995) there are described and claimed basic dyestuffs having the general formula:—



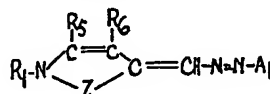
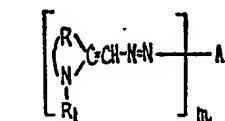
(I)

- 15
$$\left[\begin{array}{c} R \\ \diagup \\ C \\ \diagdown \\ R_1 \end{array} - CH - N \begin{array}{c} R_2 \\ \diagup \\ N \end{array} \right]_{m}^{m+} A X^{m-}$$

wherein R is the residue of a 5- or 6-membered heterocyclic ring, R₁ an alkyl, aralkyl or aryl residue, R₂ is an alkyl, cycloalkyl or aralkyl residue, A is a mono- or bivalent residue of an aromatic or heterocyclic amine, X is an acid radical and *m* is 1 or 2. These dyestuffs can be prepared by reacting dyestuff bases having the general formula:—

wherein X has the above-stated significance, A₁ denotes an aromatic or heterocyclic radical, 40 R₁ stands for a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl radical, R₂ denotes an alkyl, alkenyl, cycloalkyl, aralkyl or aryl radical, R₃ and R₄ represent hydrogen atoms or substituents, which may also be a part of 45 a condensed ring, and Z denotes a bivalent group which completes the heterocyclic ring to form a 6-membered ring.

The dyestuffs, with the exception of those where in R_2 denotes a hydrogen atom and R_1 , an aryl radical, can be obtained by reacting dyestuffs of the general formula:—

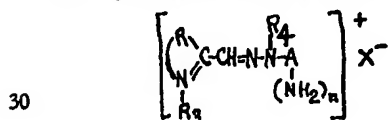


(II)

- 25 wherein R, R₁, A and m have the above-stated significance, with quaternising agents.
In Specification No. 27,467/60 (Serial No. 915,139), there are described and claimed basic dyestuffs of the general formula:—

wherein R_1 , R_2 , R_3 , Z and A , have the above-stated significance, with quaternising agents of the general formula R_4X , in which R_4 and X have the same meanings as above, in the presence or absence of a solvent or diluent.

The dyestuffs of the formula (II) serving as starting materials are obtainable, for example, in such a manner that diazotised carbocyclic or heterocyclic amines are coupled with heterocyclic methylene compounds of the general formula:—



[Price 4s. 6d.]

PATENT SPECIFICATION

NO DRAWINGS

924601



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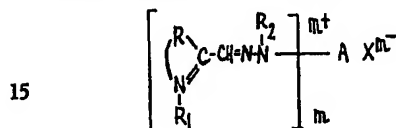
COMPLETE SPECIFICATION

Basic Heterocyclic Azo Dyestuffs

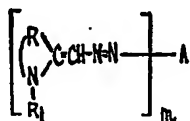
We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 22c Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention is concerned with new basic dyestuffs and with the production thereof.

In Specification No. 27,393/58 (Serial No. 875,995) there are described and claimed basic dyestuffs having the general formula:—

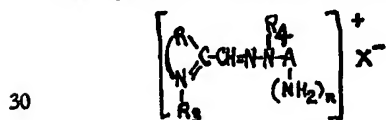


wherein R is the residue of a 5- or 6-membered heterocyclic ring, R₁ an alkyl, aralkyl or aryl residue, R₂ is an alkyl, cycloalkyl or aralkyl residue, A is a mono- or bivalent residue of an aromatic or heterocyclic amine, X is an acid radical and m is 1 or 2. These dyestuffs can be prepared by reacting dyestuff bases having the general formula:—



25 wherein R, R₁, A and m have the above-stated significance, with quaternising agents.

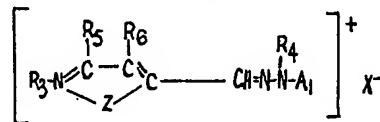
In Specification No. 27,467/60 (Serial No. 915,139), there are described and claimed basic dyestuffs of the general formula:—



[Price 4s. 6d.]

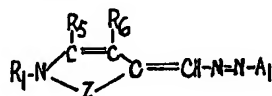
wherein R, A and X have the above-stated significance, R₃ represents hydrogen, an alkyl, cycloalkyl, aralkyl or aryl residue, R₄ denotes alkyl, aralkyl, aryl or cycloalkyl and n denotes the number 1, 2 or 3.

The basic dyestuffs of the present invention may be represented by the general formula:—



(I)
wherein X has the above-stated significance, A₁ denotes an aromatic or heterocyclic radical, R₃ stands for a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl radical, R₄ denotes an alkyl, alkenyl, cycloalkyl, aralkyl or aryl radical, R₅ and R₆ represent hydrogen atoms or substituents, which may also be a part of a condensed ring, and Z denotes a bivalent group which completes the heterocyclic ring to form a 6-membered ring.

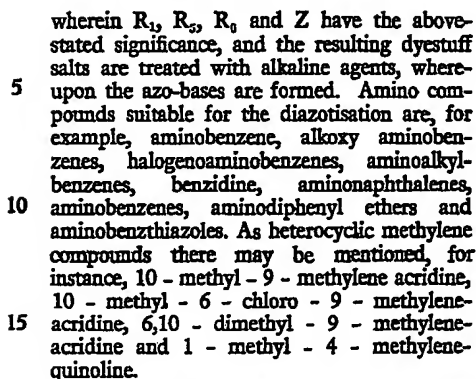
The dyestuffs, with the exception of those wherein R₃ denotes a hydrogen atom and R₄ an aryl radical, can be obtained by reacting dyestuffs of the general formula:—



(II)
wherein R₁, R₅, R₆, Z and A₁ have the above-stated significance, with quaternising agents of the general formula R₄X, in which R₄ and X have the same meanings as above, in the presence or absence of a solvent or diluent.

The dyestuffs of the formula (II) serving as starting materials are obtainable, for example, in such a manner that diazotised carbocyclic or heterocyclic amines are coupled with heterocyclic methylene compounds of the general formula:—

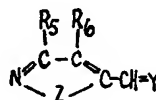
55
60


$$R_1-N=C(R_5)-C(R_6)=C-CH=Y$$
$$\text{H}_2\text{N}-\text{NH}-\text{A}_1$$

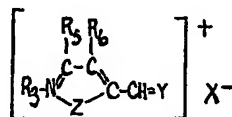
As quaternising agents for the conversion of the dyestuffs of the formula (II) into the dyestuffs of formula (I), according to the invention, there may be mentioned, by way of example, dimethyl sulphate, diethyl sulphate, toluene-sulphonic acid-esters, benzyl bromide or methyl iodide; they are preferably employed in suitable solvents, such as acetone, ligroin, benzine, benzene, toluene, chlorobenzene or chloroform.

Such acyl-amino groups may be converted into the amino groups after alkylation of the azo group according to the usual methods, for example, by splitting off the acyl residue in an aqueous or alcoholic medium at an elevated temperature in the presence of acids, such as sulphuric acid, hydrochloric acid, phosphoric acid, 4-toluene-sulphonic acid or an alkyl sulphuric acid.

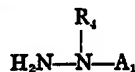
(III)



(IV)



(V)



In accordance with his process, it is also possible to obtain, *inter alia*, those dyestuffs wherein (a) R₂ denotes hydrogen and (b) R₁ denotes aryl, when (a) starting with compounds of the formula (III) and carrying out a usual salt formation in the reaction products by the action of hydrogen acids, or (b) employing diarylhydrazones of the formula (IV).

Compounds of the formulae (III) and (IV) which may be used for carrying out this modified process are, for example, pyridine-4-aldehyde, quinoline-4-aldehyde, 6-chloroquinoline-4-aldehyde, acridine-9-aldehyde, 6-chloroacridine-9-aldehyde, as well as the azomethines from 1,4-dimethylquinolinium-methosulphate, 6-chloro-1,4-dimethylquinolinium-methosulphate,

6-methoxy-1,4-dimethylquinolinium-methosulphate, or 9,10-dimethyl-acridinium-methosulphate, and 4-nitroso-dimethyl-aniline.

- 5 As examples of hydrazine compounds of the formula (V) there may be mentioned N-phenyl-N-methyl-hydrazine, N-phenyl-N-ethyl-hydrazine, N-phenyl-N-benzyl-hydrazine, N,N-diphenyl-hydrazine, N-4-methylphenyl-N-methyl-hydrazine, N-4-methoxyphenyl-N-methyl-hydrazine and N-4-chlorophenyl-N-methyl-hydrazine.

- 15 If aldehyde compounds are employed for the formation of hydrazines, the reaction can be carried out in the absence or in the presence of a solvent, such as alcohol or dilute hydrochloric acid or acetic acid; if azomethines are employed, the presence of acids, such as hydrochloric acid, sulphuric acid or phosphoric acid is essential. The reaction of the free hydrazone bases with quaternising agents, such as dimethyl sulphate, diethyl sulphate, 4-toluene-sulphonic acid esters, benzyl bromide or methyl iodide, is preferably carried out in an inert solvent, such as acetone, ligroin, benzene, benzene, toluene, chlorobenzene or chloroform.

- 20 The new basic dyestuffs are suitable for dyeing a wide variety of types of materials, such as textiles, paper or leather. It has also been found that the dyestuffs free from sulphonic acid or carboxylic acid groups yield, on materials from polyacrylonitrile, dyeings which are distinguished by good fastness properties, for example to light and to wet processing.

- 25 The following Examples are given for the purpose of illustrating the present invention, the parts being parts by weight:—

EXAMPLE 1

- 28.9 parts of the dyestuff base obtained by coupling diazotised 4-anisidine with 10-methyl-9-methyleneacridine and treating the dyestuff salt with dilute sodium hydroxide solution are dissolved, with warming, in 100 parts chlorobenzene and treated dropwise with 11.7 parts dimethyl sulphate. The reaction mixture is then heated to 100°C. and stirred on a boiling water bath for 3 hours. Thereafter, the mixture is treated with 1000 parts water and the chlorobenzene distilled off by steam. It is now clarified with active charcoal, steam is again briefly introduced, the product filtered and salted out with 104 parts sodium chloride. The dyestuff, filtered off by suction, is washed with a solution of sodium chloride, then dissolved again in boiling water and salted out with sodium chloride.
- 60 The dyestuff dyes polyacrylonitrile materials a reddish-blue shade with very good fastness properties.

Dyestuffs having similarly good properties are obtained when dyestuff bases are used

which are prepared with aniline, 4-toluidine or 4-aminoacetanilide as diazo component.

EXAMPLE 2

78.5 parts quinoline-4-aldehyde are dissolved, with warming, in 200 parts methanol and treated dropwise at 35°C. with 54 parts phenylhydrazine, whereupon the temperature rises to 57°C. After completion of the exothermic reaction, the mixture is heated to boiling, allowed to boil under reflux for 2 hours and then cooled. Quinoline-4-aldehyde-phenylhydrazone thereby separates out as pale yellow crystals which melt at 168—172°C. after recrystallisation from a mixture of alcohol and acetonitrile.

A suspension of 25.7 parts of this hydrazone in 150 parts toluene is boiled under reflux for 10 minutes, then cooled to 80°C. and treated dropwise with 13.2 parts dimethyl sulphate. The mixture is then again heated to 100°C. and stirred on a boiling water bath for 3 hours. After cooling, the separated reaction product is filtered off by suction and for further purification dissolved in 1000 parts water, the solution is clarified with animal charcoal and, after cooling, salted out with sodium chloride.

25.3 parts of the chloride of 1-methyl-quinoline-4-aldehyde-phenylhydrazone thus obtained are ground with 35 parts of a 10% sodium carbonate solution and added to 500 parts water. The mixture is stirred at room temperature for about 12 hours, then warmed to 40°C. and stirred at 40°C. for another 2 hours; the resulting precipitate is then filtered off by suction, washed with 1000 parts water at 40°C. and recrystallised from methanol.

8.6 parts of the dyestuff base thus obtained with m.p. 114—116°C(decomp) are dissolved, with warming, in 100 parts toluene, treated dropwise with 4.2 parts dimethyl sulphate and then heated to 100°C. The separated alkylated dyestuff salt is induced to crystallise by rubbing. It is heated on a boiling water bath for another 3 hours, the reaction product cooled and filtered off by suction. The dyestuff is then dissolved in 600 parts water, clarified with animal charcoal and salted out with sodium chloride.

The dyestuff dyes polyacrylonitrile fibres a slightly reddish-orange shade which is distinguished by excellent fastness to light.

EXAMPLE 3

42.7 parts pyridine-4-aldehyde are dissolved in 100 parts methanol, slight warming occurring. The solution is again cooled to room temperature and 48.7 parts of monomethyl phenyl-hydrazine are then added dropwise. The temperature thereby rises to 55°C. After completion of the exothermic reaction, the mixture is heated to boiling and boiled under reflux for 2 hours. The solvent is distilled off *in vacuo* and the residue recrystallised from cyclohexane. 21.1 parts pyridine-4-

aldehyde-phenylmethylhydrazone (m.p. 79—82°C.) thus obtained are then dissolved in 1000 parts boiling water with the addition of 18 parts concentrated hydrochloric acid (d 1.19), the solution clarified with animal charcoal and, after cooling, the dyestuff is salted out with sodium chloride.

The dyestuff materials from polyacrylonitrile in reddish-yellow shades having good fastness properties.

When using in the preceding Example, N,N-diphenylhydrazine instead of N-phenyl-N-methyl-hydrazine, but otherwise proceeding in the same manner, pyridine-4-aldehydediphenyl-hydrazone (m.p. 133—136°C.) is obtained which can be converted into the dyestuff salt by the method described above. With the same result, N - phenyl - N - benzyl-hydrazine, N - phenyl - N - butyl - hydrazine or N - phenyl - N - chloroethyl hydrazine can also be employed instead of N - phenyl - N - methyl hydrazine; dyestuffs are obtained which dye materials from polyacrylonitrile in very fast, reddish-yellow shades.

EXAMPLE 4

21.1 parts pyridine - 4 - aldehyde - phenyl-methylhydrazone prepared according to the instructions of Example 3 are dissolved in 150 parts toluene and treated dropwise with 13.2 parts dimethyl sulphate. The quaternisation product thereby separates out as crystals. The reaction mixture is heated to 100°C., stirred on a boiling water bath for 3 hours and the dyestuff isolated after previously cooling the crystal slurry. For further purification, the dyestuff is dissolved in boiling water, clarified with animal charcoal and, after cooling, salted out with sodium chloride. The dyestuff dyes polyacrylonitrile fibres in yellow shades having excellent fastness to light.

If pyridine - 4 - aldehyde - diphenyl-hydrazone (m.p. 133—136°C) is used instead of pyridine - 4 - aldehyde - phenylmethyl-hydrazone, but otherwise proceeding in the same manner, a dyestuff is obtained which dyes materials from polyacrylonitrile a very fast reddish-yellow shade.

EXAMPLE 5

78.5 parts quinoline-4-aldehyde are dissolved, with warming, in 60 parts alcohol and treated dropwise with 63.0 parts N-methyl-N-phenyl hydrazine. The reaction mixture is then heated to boiling with stirring under reflux for 3 hours and cooled. The bright yellow crystals of quinoline - 4 - aldehyde-phenylmethyl-hydrazone thereby separating out are recrystallised from a mixture of methanol and ethanol; they then melt at 131—133°C. 26.1 parts quinoline-4-aldehyde-phenyl-methyl-hydrazone are now dissolved, with warming, in 1000 parts glacial acetic acid and the solution poured into 3000 parts boiling water which contain 18 parts concentrated hydrochloric acid (d 1.19). The product is clarified with animal charcoal and,

after cooling, salted out with sodium chloride.

The dyestuff dyes materials from polyacrylonitrile a slightly reddish-orange shade having very good fastness properties.

When using, in the above Example, N,N-diphenyl hydrazine instead of N-phenyl-N-methyl hydrazine, but otherwise proceeding in the same manner, quinoline-4-aldehydediphenyl hydrazone (m.p. 143—146°C.) is obtained which can be converted into the dye salt by the method described above. With the same result, N - phenyl - N - benzyl hydrazine, N - phenyl - N - ethyl hydrazine or N - phenyl - N - cyclohexyl hydrazine can also be employed instead of N-phenyl-N-methyl hydrazine. Dyestuff salts are obtained which dye materials from polyacrylonitrile a slightly reddish-orange shade possessing excellent fastness properties.

EXAMPLE 6

26.1 parts quinoline - 4 - aldehyde - phenyl-methyl hydrazone, prepared according to the instructions of Example 5, are dissolved, with warming, in 150 parts toluene and treated dropwise with 13.2 parts dimethyl sulphate. The reaction mixture is slowly heated to boiling and the quaternisation product induced to crystallise by rubbing. The mixture is then kept on a boiling water bath for 3 hours and, after cooling, the precipitate filtered off by suction. The separated dyestuff is dissolved in 1000 parts boiling water, clarified with animal charcoal and, after cooling, salted out with sodium chloride.

The dyestuff dyes polyacrylonitrile materials a slightly reddish-orange shade having excellent fastness to light.

If quinoline - 4 - aldehyde - diphenyl-hydrazine (m.p. 143—146°C.) is employed instead of quinoline - 4 - aldehyde - phenyl-methyl-hydrazone, but otherwise proceeding in the same manner, a dyestuff is obtained which dyes polyacrylonitrile materials a slightly reddish-orange shade with very good fastness to light.

EXAMPLE 7

8.3 parts acridine-9-aldehyde and 4.9 parts N-phenyl-N-methyl hydrazine are added to a mixture of 50 parts 10% hydrochloric acid and 100 parts water. The mixture is then heated to 100°C. and stirred on a boiling water bath for 2 hours. The reaction product is introduced into a mixture of 1000 parts boiling water and 20 parts glacial acetic acid, the solution treated with animal charcoal, filtered, cooled and salted out with sodium chloride. The dyestuff thus obtained is again dissolved in 1000 parts boiling water previously treated with 5 parts concentrated hydrochloric acid and, after cooling, salted out with sodium chloride.

The dyestuff dyes polyacrylonitrile yarns and fabrics from an acid liquor a reddish-violet shade having very good fastness properties.

EXAMPLE 8

6 Parts of the salt of acridine-9-aldehyde-phenylmethyl hydrazone obtained according to Example 7 are dissolved, with warming, in 100 parts alcohol and the solution then poured, with stirring, into a mixture of 500 parts water and 20 parts of a 10% sodium hydroxide solution. The mixture is stirred for another 3 hours, the precipitated, free, yellowish-brown hydrazone base filtered off by suction and washed with water until the filtrate running off is neutral. After recrystallisation from dioxane, the base melts at 213—216°C.

3.6 parts of the acridine - 9 - aldehyde-phenylmethyl-hydrazone base thus obtained are dissolved, with warming, in 50 parts toluene, treated dropwise, with 1.6 parts dimethyl sulphate and then warmed to 100°C., the quaternisation product soon separating out as crystals. The mixture is heated on a boiling water bath for another 3 hours, cooled, the separated reaction product filtered off with suction and dissolved in 250 parts boiling water. It is then clarified with animal charcoal, allowed to cool, and salted out with sodium chloride.

The dyestuff thus obtained dyes polyacrylonitrile fibres a bluish-violet having very good fastness properties.

EXAMPLE 9

10.6 parts pyridine - 4 - aldehyde - phenylmethyl-hydrazone are dissolved, with warming, in 50 parts toluene and the reaction mixture treated dropwise with 6.6 parts allyl bromide. The solution, which is subsequently heated to boiling, starts to separate out the crystalline dyestuff at 64°C. It is allowed to boil under reflux for 6 hours, then cooled and the alkylated dyestuff filtered off by suction. It dyes materials from polyacrylonitrile a yellowish-orange very fast to light.

EXAMPLE 10

10.6 parts pyridine - 4 - aldehyde - phenylmethyl hydrazone are heated to 140°C., together with 40 parts of benzyl chloride, and stirred at this temperature for 5 hours. The reaction mixture is then transferred to a steam distillation flask and treated with 500 parts water. The excess benzyl chloride is distilled off by steam and the residual solution of the dyestuff, after clarifying with animal charcoal, filtered whilst hot and salted out with 6% sodium chloride. The isolated dyestuff can be further purified by dissolving in water, repetition of clarifying with active charcoal and salting out with 5% sodium chloride. It dyes polyacrylonitrile yarns and fabrics a reddish-yellow shade having very good fastness properties.

If ω -chloroacetophenone is employed instead of benzyl chloride, but otherwise proceeding in the same manner, a dyestuff is obtained which also dyes materials from polyacrylonitrile a very fast reddish-yellow shade.

EXAMPLE 11

13.1 parts quinoline - 4 - aldehyde - phenylmethyl-hydrazone are dissolved, with warming to 72°C., in 100 parts toluene. 8.1 parts diethyl sulphate are added to this solution which is then heated to 100°C. After stirring on a boiling water bath for three hours, the reaction mixture is cooled and the separated dyestuff filtered off with suction. It can be still further purified by clarifying with active charcoal and precipitating with 6% sodium chloride. It dyes polyacrylonitrile materials with a reddish-orange shade with very good fastness to light and wetting.

EXAMPLE 12

13.1 parts quinoline - 4 - aldehyde - phenylmethyl-hydrazone and 15 parts isopropyl iodide are sealed into a bomb tube and heated to 130°C. for 3 hours in a Carius furnace. After cooling, the reaction product is transferred to a steam distillation flask and 2000 parts of water added. Excess isopropyl iodide is distilled off by steam. The dyestuff is separated out from the filtrate with 4% sodium chloride. It dyes polyacrylonitrile fibres a slightly reddish-orange shade with very good fastness to light.

If butyl bromide is used instead of isopropyl iodide, but otherwise proceeding in the same manner, a dyestuff is obtained which also dyes polyacrylonitrile fibres an orange shade fast to light.

EXAMPLE 13

A mixture of 13.4 parts quinoline-4-aldehyde - phenylmethyl - hydrazone and 40 parts 4-chlorobenzyl chloride is heated, with stirring, to 140°C. for 5 hours. 2000 parts water are then added thereto and the excess 4-chlorobenzyl chloride distilled off by steam. The residual solution of the dyestuff is filtered whilst hot and the dyestuff salted out from the filtrate with 1% sodium chloride. For purification, the product is dissolved in 4000 parts water, clarified with active charcoal and precipitated with 1% sodium chloride. The dyestuff dyes polyacrylonitrile materials a fast orange shade.

EXAMPLE 14

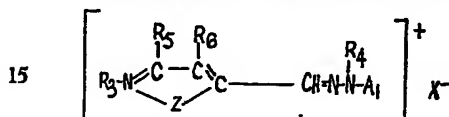
9.8 parts acridine-9-aldehyde are dissolved, with warming, in 50 parts alcohol and 8.7 parts N,N-diphenyl hydrazine are added to it. The solution is then heated to boiling under reflux for 4 hours, whereby crystals separate. After cooling the reaction mixture, the crystals are filtered off by suction and recrystallised from 90 parts dioxane. The acridine - 9 - aldehyde - diphenyl hydrazone thus obtained melts at 214—218°C.

10.3 parts acridine-9-aldehyde-diphenylhydrazone are stirred on a boiling water bath for 10 minutes with 50 parts toluene. 3.5 parts dimethyl sulphate are then added dropwise to the reaction mixture and heating on a boiling water bath is continued for another

3 hours. After the supernatant toluene has been poured off, the dyestuff is dissolved in 1500 parts water and 50 parts glacial acetic acid. Active charcoal is added to the solution, the latter filtered and the dyestuff is salted out with 6% sodium chloride. For further purification, the dyestuff is dissolved in 1500 parts water, clarified with active charcoal and salted out with 2% sodium chloride. This dyestuff dyes polyacrylonitrile fibres a violet shade which is very fast to light.

WHAT WE CLAIM IS:—

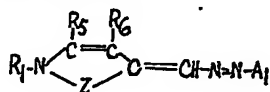
1. Basic dyestuffs of the general formula:—



wherein X is an acid residue, A_1 is an aromatic or heterocyclic radical, R_3 is a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl radical, R_4 is an alkyl, alkenyl, cycloalkyl, aralkyl or aryl radical, R_5 and R_6 are hydrogen atoms or substituents, which may also be a part of a condensed ring, and Z is a bivalent group which completes the heterocyclic ring to form a 6-membered ring.

2. Basic dyestuffs of the general formula given in claim 1, which are hereinbefore specifically mentioned.

3. Process for the production of dyestuffs of the general formula given in claim 1, except wherein R_3 is a hydrogen atom and R_4 is an aryl radical, wherein a dyestuff of the general formula:—



in which R_1 is alkyl, cycloalkyl, aralkyl or aryl, is reacted with a quaternising agent of the general formula R_4X , in which R_4 and X have the same meanings as above.

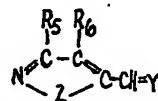
4. Process according to claim 3, wherein the reaction is carried out in the presence of a solvent or diluent.

5. Process according to claim 4, wherein the solvent is acetone, ligroin, benzene, benzene, toluene, chlorobenzene or chloroform.

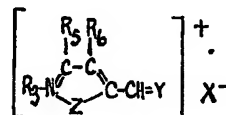
6. Process according to any of claims 3 to 5, wherein the quaternising agent is dimethyl sulphate, diethyl sulphate, a toluene sulphonic acid ester, benzyl bromide or methyl iodide.

7. Process according to any of claims 3 to 6, wherein the residue A contains one or more acylamino groups which groups are, if desired, converted into amino groups by hydrolysis, after alkylation of the azo group.

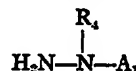
8. Process for the production of dyestuffs of the general formula given in claim 1, wherein a compound of the general formula:—



or



wherein Y is oxygen or the residue of an aromatic amine and R_3 , R_5 , R_6 , X and Z have the same meaning as above, is reacted with a hydrazine compound of the general formula:—



wherein A_1 and R_4 have the same meaning as above, and the resultant hydrazone reacted in the form of the free base or in the form of a salt with a quaternising agent of the general formula R_4X , in which R_4 and X have the same meanings as above, and, in the case where the residue A_1 contains acylamino groups, these are, if desired, converted into amino groups by hydrolysis.

9. Process for the production of dyestuffs of the general formula given in Claim 1, substantially as hereinbefore described and with reference to any of the specific Examples.

10. Dyestuffs of the general formula given in claim 1, whenever prepared by the process according to any of claims 3 to 9.

11. Materials made from polyacrylonitrile, whenever dyed or printed with a dyestuff of the general formula given in claim 1.

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